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Reduction chemistry of neptunium cyclopentadienide complexes: from structure to understanding

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Neptunium complexes in the formal oxidation states II, III, and IV supported by cyclopentadienyl ligands are explored, and significant differences between Np and U highlighted as a result. A series of neptunium(III) cyclopentadienyl (Cp) complexes [Np(Cp)],[ its bis-acetonitrile adduct [Np(Cp)(NCMe)],[ plus its Kcp adduct K[Np(Cp)] and [Np(Cp)] (Cp = C5H5SiMe3) have been made and characterised providing the first single crystal x-ray analyses of Np Cp complexes. In all NpCp, derivatives there are three Cp rings in η1-coordination around the Np4+ centre; additionally in [Np(Cp)] and K[Np(Cp)] one Cp ring establishes a μ-η1-interaction to one C atom of a neighbouring Np(Cp) unit. The solid state structure of K[Np(Cp)] is unique in containing two different types of metal-Cp coordination geometries in the same crystal. Np4+(Cp) units are found exhibiting four units of η1-coordinated Cp rings like in the known complex [Np5(Cp)4], the structure of which is now reported. A detailed comparison of the structures gives evidence for the change of ionic radii of ca. 8 pm associated with change in oxidation state between Np4+ and Np5+. The rich redox chemistry associated with the syntheses is augmented by the reduction of [Np(Cp)] by KCp in the presence of 2.2.2-cryptand to afford a neptunium(II) complex that is thermally unstable above -10 °C like the U4+ and Th4+ complexes K{2.2.2-cryptand}{Th(U(Cp))}. Together, these spontaneous and controlled redox reactions of organo-neptunium complexes, along with information from structural characterisation, show the relevance of organometallic Np chemistry to understanding fundamental structure and bonding in the minor actinides.

Introduction

Fifty years have passed since the foundation of organometallic neptunium chemistry in the form of cyclopentadienyl chemistry,1 and yet only a handful of complexes have been reported, and even fewer fully characterised.2,4 Yet increasingly, combined synthetic/spectroscopic/computational studies are demonstrating how covalently binding, soft, carbocyclic organometallic ligands that form actinide-ligand σ-, π-, δ- and even η-(back)bonding interactions provide an excellent platform for advancing the fundamental understanding of the differences in orbital contributions and covalency in f-block metal — ligand bonding.5 Understanding the subtleties are key to the safe handling and separations of the highly radioactive nuclei.6,8 For example, recent quantitative carbon K-edge X-ray absorption spectroscopy (XAS) analyses on the organometallac [An(COT)2] (An = Th, U), “actinocenes” provided the first experimental evidence for extensive η-orbital interactions in thorocene, and remarkably little in the U analogue, with contrasting trends in orbital mixing.9 Furthermore, a combination of experimental and QTAIM computational comparisons of [M(L2)X] (M = Sm, U, Np; X = Cl, I; L= dianionic arene-bridged trans-calix[2]benzene[2]pyrrole)10 showed significant differences (up to 17%) in orbital contributions to M-L bonds between the Ln and An analogues, and that the covalency in the Np-ligand bonding arises from spatial orbital overlap rather than a coincidental energy degeneracy.13 The work also demonstrated differences between U and Np in their reaction chemistry, such as the stability of the Np8 formal oxidation state or the reduction of Np14 to Np15 upon complexation.

Organoneptunium chemistry has relied heavily on the ubiquitous cyclopentadienyl ligand, Cp = (C5H5)7, as a strongly binding, sterically demanding yet flexible, monoanion, and focused almost exclusively on Np4+ complexes. The first evidence for the formation of [Np(Cp)X] (X = Cl, F) came from a radiochemical synthesis, i.e. the irradiation of a 238U complex with thermal neutrons,14 and [Np(Cp)]X (X = Cl, F) were subsequently reported from standard chemical routes as thermally robust, volatile complexes.11,12 Baumgärtner et al. reported the first homoletic organoneptunium complex, tetrakis[η5-cyclopentadienyl]neptunium(IV), [Np(Cp)4], from treatment of NpCl4 with excess KCp in benzene.15 Many of the earliest studies on neptunium cyclopentadienyl complexes also had the aim of exploring covalency in the bonding, using the fact that Np is a Mössbauer active nucleus. However, not all
the studies agreed. The first Mössbauer studies on [Np(Cp)] and [Np(COT)] suggested less interaction in between the central ion and the Cp ligands but appreciable covalency in the Np-COT bonding. On the other hand, Bohlander reported the isomer shift of the Np nucleus in [Np(Cp)] closely approaches that of the record-breaking, covalent [Np(COT)], thus being the most covalent Np-Cp derivative. Finally, from analysis of the isomer shifts Karraker stated that there were smaller covalent bonding contributions in [Np(Cp)] than [Np(Cp)Cl], whereas Adrian concluded the opposite. The redox properties of the element play a pivotal role in neptunium chemistry as it conventionally exhibits five oxidation states in compounds, from +3 to +7. Recently, we reported that a formally Np(V) complex NpL3 supported by C4Me6, the trans-calix[2]benzene[2]pyrrole was accessible; black solutions were sufficiently stable (up to 90 minutes) for spectroscopic analyses but crystals were too small for single crystal diffraction analyses. Somewhat surprisingly, given the increased stability of the Np(V) oxidation state compared to U(VI), this work was also the first to report single crystal structural characterisation of a series of Np(Cp)Cl complexes. To date, the only organometallic Np(V) complexes characterised by single crystal X-ray diffraction are neptunocenes [Np(C6H5)2]2, [Np(Cp)Cl(OPPh3)2], [Np(Cp)(OPh)], and two examples of the Cp,Np-functionalised adduct [(UO2)(THF)2H2L] (L = ‘Pacman’ Schiff-base polymeric macrocycle),3 in which we studied the Np-Np coordination to one oxo group of the uranyl dication to compare the degree of electron transfer via the oxo-bridge between U, Np, and Pu cations. Structurally characterised Np(V) organometallics are still limited to the [M(L4)X] complexes we reported.4 Modern characterising data including 1H NMR spectroscopic data have been reported for just a couple of complexes.

Many routes to solvated and base-free U(VI)(Cp)3 complexes exist, but only the THF solvate of [Np3(Cp)3] has been reported to date, and was made from treating [Np3(Cp)3Cl] with potassium metal and catalytic naphthalene in refluxing THF for a few days. The product was first assigned as the tris THF solvate [Np3(Cp)3(THF)]14 but subsequent IR, FIR and UV-vis-NIR spectroscopic analyses suggested the constitution of an 1:1 Lewis base adduct [Np3(Cp)3(THF)] analogously to that of uranyl. Attempts to desolvate it by heating samples in vacuo led to significant decomposition.4

Herein, we report the synthesis and structural characterisation of a series of Np(V) cyclopentadienyl complexes, and their reduction chemistry, both spontaneous and directed. Structural changes are discussed in relation to the neptunium formal oxidation state and nature of the ligands, as the majority of the complexes have been structurally characterised by single crystal X-ray diffraction.

### Results

#### Syntheses

All the syntheses start from NpCl3. This can be directly transformed into [Np3(Cp)3], Np3Cp by the reaction of NpCl3 with an excess of KCp in toluene.23 Single crystals of Np3Cp grow in the supernatant during a prolonged extraction of the crude product with pentane. The spectroscopic data agree with the literature reports.12, 23 Np3Cp itself can be - from a reaction with NH4C2O2, 12 - converted to [Np3Cp]Cl, Np3CpCl which is an ideal starting material for the synthesis of [Np3]2, Np3Cp. The reduction of Np3Cp by Na/Hg in EtOH affords Np3Cp as its diethyl ether solvate [Np3Cp2(ET2O)], Scheme 1. This solvent molecule is labile and can be easily removed in vacuum to afford the solvent free Np3Cp which is only sparingly soluble in non-coordinating solvents due to the polymeric nature of the molecular structure (see below) but dissolves slowly in Et2O, THF, or MeCN, again forming solvates [Np3Cp2(ET2O)], [Np3Cp2(THF)], or [Np3Cp2(NCMe)2], respectively.

### Scheme 1. This solvent extraction into neptunium complexes presented in this work. Np3Cp is obtained by reduction from Np3CpCl and readily forms the MeCN stabilised solvate. The silylated analogue [Np3Cp'](Cp' = C5H5SiMe3) is better obtained from the reaction of Np3Cl3 with KCp and can be reduced to its K salt. Dotted lines indicate laboratory procedures. Key: (i) excess KCp, PhMe; (ii) Na/Hg, Et2O, -NCl; (iii) KCl; (iv) Na/Hg, Et2O, -NaCl; (v) MeCN; (vi) KCl, 2.2.2-cryptand, THF/ET2O, -8C.

Crystals of [Np3Cp2(ET2O)] could not be analysed via X-ray diffraction as during the crystal mounting procedure they lose coordinated ET2O solvent molecule readily. Similarly, no stable adducts of a lanthanide analogue [Ln(Cp)3(OT2)] has yet been reported. However, single crystals of the bis-acetonitrile adduct [Np3Cp2(NCMe)2] have been grown from acetonitrile solution at RT and studied by X-ray diffraction.

The reaction of Np3CpCl with 1.1 equiv. of KCp in THF does not lead to the simple Cl substitution product Np3Cp. After 4 d reflux and evaporation of the solvent, Np-pentane extraction recovered half of the starting material Np3CpCl (49 %), and a subsequent extraction with Et2O afforded maroon single crystals of the new, reduced, Np(V) complex K[Np(Cp)3], K[Np3Cp] in 37 % yield. When the reaction is repeated without heating the mixture, no soluble, molecular product can be isolated.

For the synthesis of [Np(C6H5SiMe3)3], Np3Cp another reaction pathway was followed as no starting material [Np(C6H5SiMe3)]Cl was available: Np3Cp is generated in situ from the reaction between NpCl3 and excess Na(Hg) in diethyl ether at room temperature. The reaction between this NpCl3 and three equivalents of K(C6H5SiMe3) in diethyl ether at room temperature afforded the target Np3Cp. Green, crystalline Np3Cp is deliquescent under 1 atm of N-pentane vapour at the neptunium formal oxidation state and nature of the ligands, as the majority of the complexes have been structurally characterised by single crystal X-ray diffraction.
room temperature but single crystals can be isolated reproducibly by evaporation and cooling of pentane solutions. The reduction of a solution of NpCp₃ with KC₈ was carried out similarly to the method originally described for the synthesis of the thermally unstable [K(2.2.2-cryptand)][U(C₅H₅)₂SiMe₃]₂ by Evans et al., but the crystallization temperature maintained lower, at -78 °C. A previous reduction of NpCp₃ confirmed that no compound could be isolated even at the coldest achievable reaction temperatures. In THF/Et₂O the mixture immediately turns very intense dark brown on contact with the solid reducing agent, and small, shiny black crystallites with the assumed composition K(2.2.2-cryptand)[NpCp₃] appear in the filtrate after approx. 1h of storage at -78 °C. Several potentially single crystals of suitable size for an X-ray diffraction study were analysed but only very weak diffraction was observed as the crystals had degraded during the radiologically protective mounting procedure. Due to the high sensitivity of the compound we were not able to determine the structure of the reduced product from this reaction or to measure

Spectroscopy

The ¹H and ¹³C gHMOC NMR spectra of NpCp₃ in THF-d₈ show only one resonance for the Cp ring protons at δₚ = -9.65 ppm and the respective ¹³C shift of δC = 150.4 ppm. The ¹H NMR spectrum of NpCp₃ in toluene-d₈ solution contains three paramagnetically contact-shifted resonances between -1.38 ppm (the SiMe₃ protons) and -9.51 ppm in a 9:2:2 ratio, implying the identical bonding mode of the three ligands. The spectrum acquired in THF-d₈ solution appears similar, the resonances are slightly shifted downfield (δₚ = -0.6 to -9 ppm) suggesting an interaction with the THF solvent. The ¹H NMR spectrum of the sparingly soluble K[NpCp₃] in THF-d₈ contains one broad resonance at -11.9 ppm, again showing the identical coordination behaviour of the Cp rings in solution. The solubility of K[NpCp₃] in THF is however too low to observe measurable absorptions in the UV-vis-NIR spectra.

For the Np³⁺ complexes, all the Cp ring proton resonances are observed at ca. -10 ppm suggesting an electronically similar environment in each complex. When no correlated spectra are reported here then the complex decomposes in the fluoropolymer NMR-tube liners prior the spectra could be recorded.

The ATR spectrum of NpCp₃ features several characteristic vibrations of the Cp rings, which correlate well with the previously reported IR data of the complexes [M(Cp)₃] (M = U, Pu, Am, and Tm)⁵⁶. Indeed, the similarity of the values of the entire series shows the very comparable constitution of the complexes. The most characteristic bands are the set of four absorptions at 666, 611, 581 and 519 cm⁻¹.⁵⁷ ATR-FTIR spectra of K[NpCp₃] show very similar Cp ring vibrations to those previously described for NpCp₃ with a slight shift to lower energy of the vibrations in K[NpCp₃] vs. NpCp₃ agreeing with the higher overall negative charge in the complex K[NpCp₃].

Molecular structures

The molecular structure of NpCp₃ is here reported for the first time. Dark red single crystals were obtained by extraction with pentane over several days. The compound is kinetically stable. X-ray diffraction analyses revealed an ideal tetrahedral environment of the Np center, shielded with the four Cp rings in an isostructural complex to its Th³⁺ or U³⁺ analogue (Figure 1).

Across the row of the isostructural [AnCp₃]³⁺ (An: Th, U, Np), in line with the actinide contraction the cell volume decreases from 802 Å³ (Th) to 786 Å³ (U) to 775 Å³ (Np). Furthermore, a shrinking of the entire molecule is expressed by a decreasing An - Cp ring centroid distances. These are found to be 2.606 Å for Th, whereas in the U analogue they are determined to 2.588 Å and for the here presented Np complex they are 2.551 Å, again shorter. The shrinking parallels the decrease of the ionic radii; this implies that the nature of the bonding in the complexes in this row is comparable and even if covalency plays a role it does not affect the bond lengths in the complexes significantly.

Dark-brown, almost black single crystals of NpCp₃ suitable for X-ray crystal structure determination were obtained from a 3.5% v/v diethyl ether in n-pentane solution stored at room temperature for 7 d.
The solid-state structure of \( \text{NpCp}_3 \) shows a polymeric structure motif. All the three \( \text{Cp} \) rings are bound \( \eta^5 \) towards the central \( \text{Np}^{3+} \) atom. Due to its Lewis acidity coordinative saturation is achieved by additional \( \eta^5 \)-coordination to one of the \( \text{Cp} \) rings of another \( \text{NpCp}_3 \) unit resulting in one \( \mu-\eta^5,\eta^1 \)-coordinated bridging cyclopentadienyl group, Figure 2a, establishing an overall polymeric zig-zag structure with a \( \text{NpCp}_3 \)-molecule between \( \text{NpCp}_3 \)-molecules angle close to 170, Figure 2b. This is in agreement with the structures of isomeric \([\text{Ln(Cp)}_3]_n\) complexes. 30-33 In this coordination environment a distorted tetrahedral geometry around the \( \text{Np}^{3+} \) centre is established with a strong \( \text{Np-C} \) interaction to the \( \text{C} \)-atom to which the \( \eta^1 \) coordination is established (\( \text{Np-C} 2.815(11) \) Å) whereas the bond distance between the \( \text{Np} \) atom and the \( \text{C} \)-atom \( C2 \) is \( 3.266(9) \) Å and \( C5 \) is \( 3.552(10) \) Å which is considered to be non-bonding. The geometry around the cation in \( \text{NpCp}_3 \) is more closely aligned with the larger rare earth analogues that have more electron-rich \( \text{Cp} \) rings, \([\text{Ln} (\text{C}_5 \text{H}_5 \text{Me})_3]_n \) (\( \text{Ln} = \text{La}, \text{Ce}, \text{Nd} \)). These all show \( \mu-\eta^5,\eta^1 \)-binding for each cyclopentadienyl ligand. However, some of the published data were recorded at room temperature and are less well resolved. In order to discuss fully the differences between the isosctructural complexes of the type \([\text{M(Cp)}_3]_n \) (\( \text{M} = \text{Ln}, \text{An} \)) it will be necessary to re-determine the solid state structures of the corresponding \( \text{Ln} \) complexes.

Red-brown crystals of \( \text{K[NpCp}_3] \) suitable for single crystal X-ray diffraction analysis were grown from a diethyl ether solution stored at room temperature for \( \alpha \) ca. 100 h. The asymmetric unit consists of 1.5 molecules of \( \text{K[NpCp}_3] \) and 0.5 molecule of a heavily disordered diethyl ether molecule residing on the crystallographic \( C2 \) axis. \( \text{K[NpCp}_3] \) is also polymeric in the solid-state, with all \( \text{Cp} \) ligands forming bridging interactions of either \( \eta^5 \) to another \( \text{Np} \) atom or \( \eta^1 \) to a \( \text{K} \) or \( \text{Np} \) cation. This results in two different types of \( \text{Np} \) coordination geometry arising from the bridging modes, Figure 3. The coordination environment around the first \( \text{Np}^{3+} \) cation, labelled A, is \( \eta^5-\text{Cp})_2(\eta^1-\text{Cp}) \), which closely mirrors that of the parent complex \( \text{NpCp}_3 \); that around the second \( \text{Np}^{3+} \) cation, labelled B, is \( \eta^5-\text{Cp})_4 \) comparable to the coordination observed for the four \( \text{Cp} \) rings in \( \text{NpCp}_4 \). To our knowledge, this is the first instance of a \( \text{Cp} \) complex showing two different types of metal coordination geometries in the same crystal. This behaviour might be explained by the high coordinative flexibility of the relatively large \( \text{An} \) cations. Very few \( \text{f} \)-block complexes have comparable solid state structures. The complex \([\text{Ce(C}_5\text{H}_5\text{Me})_3]_n \) forms in the solid state with \( \eta^5,\eta^1-\text{Cp} \) anions bridging, and one uranium complex was published very recently; \( [\text{K}(2.2.2\text{-cryptand})][\text{U(Cp)}_3]_2 \), also shows an \( \eta^5-\text{Cp})_3(\eta^1-\text{Cp}) \) geometry. The An\( ^n(\eta^5-\text{Cp})-\text{M-C} \) distance is \( 2.752(7) \) Å for \( \text{Np} \) and \( 2.776(2) \) for \( \text{U} \), consistent with the ionic radius difference (six-coordinate \( \text{Np}^{3+} = 1.01 \) Å; \( \text{U}^{3+} = 1.025 \) Å).

The \( \text{Np(A)} \) and \( \text{B} \) type cations both form polymeric chain structures, which connect to each other, and into a 3D network via further K cation interactions. For \( \text{Np(A)} \), Figure 3a, there are three distinct \( \text{Cp} \) binding modes for the four \( \text{Cp} \) ligands: one \( \eta^5-\text{Np}(\eta^5-\text{Cp}) \); one \( \eta^5-\text{Np}(\eta^1-\text{Cp}) \) (for \( \text{Ct2} \)); and two \( \eta^5-\text{Np}(\eta^5-\text{Cp}) \) (for \( \text{Ct1} \) and \( \text{Ct3} \)). The second type of \( \text{Np} \), type \( \text{B} \), Figure 3b, displays \( \eta^5 \)-binding of all the \( \text{Cp} \) ligands arranged in an irregular tetrahedral fashion around the \( \text{Np}^{3+} \) centre. The average separation between the \( \text{Np} \) atoms and the \( \eta^5-\text{Cp} \) ring centroids in these molecules is slightly longer in accordance with the greater steric encumbrance at the \( \text{Np} \) centre (\( 2.635(1) \) Å in \( \text{B} \) vs. \( 2.507(5) \) Å in \( \text{A} \)). Accordingly, the \( \text{C} \)-atoms for the fourfold \( \eta^5 \)-coordinated \( \text{Np} \) centres show larger \( \text{Np-C} \) distances than \( \text{K} \) cations (like in \( \text{K} \)-metal complexes) with \( \text{Np}(\eta^5-\text{Cp})-\text{C} \) distances of \( 3.013(5) \) Å. These latter are more comparable to the coordination \( \text{Np}(\eta^5-\text{Cp})-\text{C} \) in \( \text{K(NpCp}_3) \)-coordinated \( \text{Np} \) cation (\( 2.732(13) \) to \( 2.842(9) \) A).
Figure 3. a) Thermal ellipsoid drawing of a portion of the polymeric structure type K[Np(η⁴-C₅H₅)](NCMe)₂, formed by Np⁺ ions A and B. b) The polymeric sheet-like structure type K[Np(η⁴-C₅H₅)](NCMe)₂ formed by Np⁺ ions B. The thermal ellipsoids for (a) and (b) are at 50% probability. c) Ball and stick drawing of part of the 2D polymeric sheet structure formed by the type A Np⁺ cations and K⁺. Atom colours: C (white), K (light grey), Np (dark grey), Np1 (filled with lines). Hydrogen atoms and lattice diethyl ether molecules are omitted for clarity. Symmetry generated atom names are labelled A, B and C. Selected distances [Å] and angles [°] for K[Np(C₅H₅)](NCMe)₂: Np1-C1 2.527(4), Np1-C11 2.516(4), Np1-C13 3.003(5), Np1-C14 3.013(5), K1-C13 3.067(6), K1-C14 3.013(5), K1-C9 3.197(10), Np2-C16 3.049(8), K2-C20 2.752(7), K2A-C11 3.003(5), K2A-Cl5 2.884(7), Cl1-Np1-C1 115.50(13), Cl1-Np1-C13 118.92(16), Cl2-Np1-C13 117.13(17), Cl1-Np1-C20 96.53(16), Cl2-Np1-C20 99.01(17), Cl3-Np1-C20 103.51(19), Np2-C14 2.631(5), Np2-C15 2.645(7), Cl4-Np2-C15 109.2(2), Cl4-Np2-C14 109.4(2), Cl4-Np2-C15A 110.5(2), Cl5-Np2-C15A 107.9(3), Cl4-K1-C14A 104.67(19), Cl4-Np2-C15A 107.9(3), Cl4-C14-Np2-C15A 110.5(2). Figure 4. Thermal ellipsoid drawing (50% probability for non-H atoms) of Np(C₅H₅)(NCMe)₂ in the solid state. H atoms omitted. Selected bond lengths [Å] and angles [°] for Np(C₅H₅)(NCMe)₂: Np1-N1 2.665(4), Np1-C11a 2.539(4), Np1-C12 2.540(4), N1-C11 1.133(5), C11-C12 1.465(5), Cl1-Np1-C1A 116.9(2), Cl1-Np1-C1 119.9(2), Cl1-Np1-C1A 123.5(2).

The geometry around the Np atom in the molecular structure of Np(C₅H₅)(NCMe)₂ can be generally described as distorted trigonal bipyramidal with three Cp in η⁵-coordination mode exhibiting the trigonal plane around the Np atom whereas the two MeCN ligands are forming occupying its apical positions. In the molecule there is a two-fold axis passing through the Np atom. This results in the nearby linear arrangement of the two acetonitrile ligands exhibiting a Np angle of 178.4(2)°. The low steric demand of the MeCN ligands enables a close to ideal arrangement of the three Cp rings in one plane around the Np centre showing a sum of angle of 360.3° (Ct-Np1-Ct) with a deviation out of the plane consisting of the three centres of the Cp rings plus the Np atom of less than 0.005 Å. Accordingly...
as well the bond distances between the Np atom and the centres of the Cp rings are identical with 2.539(2) and 2.540(2) Å. These findings compare well to the metrics for the series of LnCp₃(nitrile)₂ complexes that have been structurally characterised.⁴⁴⁻⁴⁶ For the actinides however, only some cationic U⁴⁺ complexes have been structurally characterised.⁴⁷ In these U⁴⁺ cationic complexes of the type UCP₂(NCR)₂* shorter bond distances are found than here for NpCp₂(NCMe)₂ (U-N distances < 2.6 Å).

All of the Np⁴⁺ centres in the above are coordinatively unsaturated in the absence of ligand bridging, but this situation can be readily changed by the use of sterically more demanding Cp ligands like C₆H₅SiMe₃ (Cp'). Olefite-green single crystals of Np(Cp')₂ suitable for X-ray diffraction analysis were obtained from cooling a concentrated n-pentane solution to -20 °C. The asymmetric unit consists of a single molecule of Np(Cp')₂. The molecular structure of Np(Cp')₂ is shown in Figure 5 and consists of the mononuclear Np⁴⁺ complex containing three η¹-bound Cp' ligands, with all the Ct(η²-Cp')-Np-Ct(η²-Cp') angles close to 120° and the average Np-Ct(η¹-Cp') distance of 2.482(3) Å. This means that in Np(Cp')₂, the Cp rings with the bulky substituents are closer to the metal than in the previously described complexes Np(Cp)(NCMe)₃, K[NpCp₃], and NpCp₃ for which Np-Ct distances of 2.51 Å and 2.54 Å are found. This means that due to the trigonal planar arrangement of the Cp' ligands with the resulting larger bond angles around the Np⁴⁺ centre in Np(Cp')₂ the metal is able to establish stronger interactions with the more electron rich Cp' ligands.

Figure 5. Thermal ellipsoid drawing (50 % probability for non-H atoms) of Np(Cp')₂ in the solid state. H atoms omitted. Selected bond lengths [Å] and angles [°]: Np1-Ct1 2.485(2), Np1-Ct2 2.481(2), Np1-Ct3 2.479(2), Np1-Cu 2.734(6) to 2.786(4), S1-(C1-C5) plane -0.382(8), S2-(C6-C10) plane -0.109(8), S3-(C11-C15) plane -0.169(8), C11-Np1-Ct2 119.86(8), C11-Np1-Ct3 120.46(7), C27-Np1-Ct3 119.06(8).

The Np1 atom in Np(Cp')₂ lies in plane of the Cp' ring centroids with only a minor out-of-plane distortion (0.113(1) Å), affording a nearly trigonal planar (O₃h) geometry which is isosctructural with the previously reported uranium complex [U(Cp')₃].⁴⁸ The average An-C distance of 2.78(4) Å (2.76(3) Å for U) and An-Ct(η²-Cp') of 2.482(3) Å (2.51(3) Å for U) are the same within standard uncertainties. However, the similarity of the values can be taken as a sign that the arrangement of the three Cp' ligands is dominated more by steric factors than by ionic radii. The ligands take a trigonal planar coordination around the Np centre, which is not only in agreement with the structure of its U analogue, but as well with the solid state structure found for the small lanthanide cation in [Yb(Cp)₃]+ or U(Cp)₃, containing complexes (where R represents a bulky hydrocarbyl group).⁴⁹, 50

Discussion
Redox reactivity
In scheme 1 there are mainly represented two reaction pathways: nucleophilic substitution at the metal centre or reduction. Np⁵⁺Cl₃ was prepared readily from the reaction of Np⁵⁺Cl₄ with excess of KCp via SN reaction. From this a Cp ligand can be abstracted by protonation and so that even Cl⁻ is able to coordinate to the metal forming Np⁵⁺(Cp)Cl.

The homoleptic complexes NpCp₂ and Np(Cp')₂ are accessible only by reduction: NpCp₃ is best produced by reduction of NpCp₃Cl whereas Np(Cp')₂ is well prepared by the in-situ formation of NpCp₃ from NpCp₄ followed by SN reaction at the metal centre leading to NpCp₃. As the silyl-substituted C₆H₅SiMe₃ anion more effectively stabilises lower oxidation state metal cations the synthesis of the first organometallic Np(II) complex succeeded by reduction of NpCp₃ with KC₆ in agreement with Evans et al.,²⁴ the crystallization temperature was lowered to -78 °C but the small, shiny black crystals appearing in the filtrate after 1h of storage at -78 °C showed too few diffraction properties.

Although the neutral complex [Np(Cp)₃] has been reported several times to be formed in the reaction between NpCl₄ and excess KCp in THF, benzene, or toluene solution, the reaction reported here between [Np(Cp)₃]Cl and KCp affords the Np⁴⁺ product K[Np(Cp)₄] giving evidence that in this case Cp acts in two roles: as reducing agent plus as stabilising ligand for the coordinatively unsaturated Np⁴⁺ ion in dependence on the reaction conditions.

These observations could provide an explanation for the disagreements in the Mössbauer studies on covalency. Adrian observed that Mössbauer spectra of the [Np(Cp)₃] targets provided by Bohlander contained two low intensity bands arising from the unidentified impurities, which may provide an argument for this study.¹² The utility of the Cp anion as a reductant is well documented in preparative inorganic chemistry, and an additional equivalent(s) of either NaCp or [MgBr(Cp)] can be conveniently employed to reduce in situ the higher oxidation state transition metal and lanthanide precursors and produce metallocenes of the M⁰ centres i.e. Cr²⁺, V³⁺, Ru⁶⁺, Os⁶⁺ or Eu⁶⁺. In actinide chemistry this reactivity is rarer, and the only reported synthesis so far is of the homoleptic complex [²³⁹Pu(Cp)₃] from treatment of [C₆H₅]₂[²³⁹PuCl₃] with excess Mg(Cp)₂.⁶⁸ However, it is pertinent to note that the salt metathesis reactions between [Np(Cp)₃]Cl, and group 1 alkyl- or aryl- anions formed only low yields of [Np(Cp)₃(R-n-Bu)] and [Np(Cp)₃Ph] (40-60 %) alongside undefined Np⁴⁺ by-products, presumably due to the homolysis of the Np⁴⁺-alkyl bond.¹², ⁶¹
The reported formal potentials summarized in Table 1 show the NpIV/NpIII couple is intermediate in value between U and Pu in the triad, as would be expected. Cyclic voltammetry experiments have demonstrated that [An(Cp)2Cl] (An = U, Np) complexes show reversible one-electron reduction processes at Ep/2 = -1.80 V (UIV/UIII) and -1.29 V (NpIV/NpIII) in THF (vs. Fc/Fc†). Early actinide elements (An = Th-U) demonstrate a clearer thermodynamic preference for the +4 over +3 oxidation state and in its organometallic chemistry, for NpIV/III the preference is more finely balanced. The electrochemical properties of actinide centres in organoactinides are usually considerably affected by ligand environments.

The disproportionation of UIII into 0.75 eq of AnIV and 0.25 eq of AnIII is well-known, and has been reported for NpIII. We used a variety of techniques to confirm the formal UIII oxidation state in the inverse sandwich complexes [(X:U):2(µ-η5:η5-CpR2)], (in which the arene carries a dianionic charge) (X = bulky aryloxide or amido monoanion, CpR2 = benzene, toluene, naphthalene, and silylated or borylated arene derivatives) that were formed from the disproportionation of UIII molecules into UIV and the formal intermediate UXII. More recently, Meyer used computational analyses to confirm the formal UIII oxidation state in the arene-supported tris(aryl oxide) ate complex [K{[2.2.2-crypt]}((µ3-κ3:κ3:κ3-ARO)3mes)]. Following the report of the +2 oxidation state for uranium in a molecular complex [K{[2.2.2-cryptand]}][UCp2] by Evans et al. and our report of the relatively stable, formally NpII complex NpL4(dme), which survives up to 90 minutes in solution and as small near-black crystals, the synthesis of the neptunium homologue [K{NpCp2}] of the U `ate-` complex seemed a reasonable target. While a convenient low-temperature route with radiological protection was devised to afford solutions and crystals of a Np(II) complex which was insufficiently thermally stable to enable characterisation of the solutions or X-ray data collection on single crystals.

This situation should be even easier moving from Np to Pu which already shows a much more stable MIII oxidation state in its complexes.

Solid state structures
All the complexes presented here, three NpIII and one NpIV, contain at least three Cp ligands in the coordination sphere of the Np, so that a structural comparison can be performed. In the structures of the NpII complexes NpCp2(NCMe)2, K[NpCp4], NpCp3, the Np centres are surrounded by three Cp rings in η5-coordination mode. In all these complexes the centre of the Cp ring is placed between 2.51 Å and 2.54 Å distant from the Np atom. However, in [K(NpCp4)] there is realised a second coordination mode of the NpIII atoms: besides the coordination known from the NpCp3 (and from the complexes LnCp2) consisting of the three already mentioned η5-coordinated Cp rings plus one bridging Cp ring establishing an additional µ-η-coordination in [K(NpCp4)] there is a NpCp unit with the Np atom surrounded by four Cp rings all in η5-coordination. This situation is comparable to the coordination found in complexes [An(Cp)2], where in the row from Th over U to Np M to centre of ring distances are found of 2.606 (Th), 2.588 (U), and 2.551 Å (Np), respectively. These values compare to the one of 2.635 Å for the four times η5-coordinated Np centres in [K(NpCp4)]. The latter systems means one can consider the difference in the ionic radii between NpIII and NpIV in an equivalent coordination environment built by in this case four η5-coordinated Cp rings to be equal to (2.635 – 2.551 =) 0.08 Å.

We note that the CN stretch in the IR spectrum of NpCp2(NCMe)2 is observed at 2262 cm-1, lower than in the corresponding U cationic complexes which have a stronger M-N interaction.

The trigonal planar arrangement of the three Cp7 ligands [Np(Cp')3] around the NpIII centre, analogous to the corresponding U complex raises the possibility that with this complex should be able to show comparable redox chemistry to that of U and Th, where the geometry provides suitable orbitals for an additional valence electron to reside. Therefore, it was used as the starting material for the organometallic Np(II) complex for reduction with KC8.

Conclusions
As could be anticipated, the synthetic chemistry of cyclopentadienyl-supported NpII and NpIV complexes is comparable to that of uranium, with the differences mainly being caused by the less negative reduction potential of the NpIV ion. For the first time a solution-based method for the quantitative formation of green, poorly soluble, but high-surface area, and therefore reactive NpCl2 has been demonstrated from reduction of NpCl5, and shown to be synthetically useful in anaerobic reactions, even in the absence of strongly coordinating solvents. Complexes NpCp3 and NpCp4 were synthesized reproducibly in high yields salt metathesis reactions from this or from more traditional reduction reactions of the known complex NpCp2Cl.

One notable example of the greater stability of the NpIII ion with respect to UIII in these complexes is the overlooked reactivity of NpCp3 with excess KCp, which results in the isolation of the first actinide(III) tetrakis-cyclopentadienyl complex, [K(NpCp4)] under the synthetic conditions previously assumed to afford only the neutral complex NpCp4. Remarkably, the solid-state structure of [K(NpCp4)] compound exhibits intra-crystal dimorphism; two different types of
NpCp₄ coordination geometries, half of the Np(V) cations are \((\eta^2-Cp)(\eta^1-Cp)\) and half are \((\eta^1-Cp)_2\), with the two different types of Np(V) forming separate polymeric chains that are bridged by potassium counter-cations to form the extended polymeric structure. Unexpectedly, this structure may answer the concerns expressed by Adrian et al. who reported two similar, but unidentified impurities in samples of NpCp₄ that they studied by Mössbauer spectroscopy. Comparison of the structures of K[Np(Cp')₃] and NpCp₄ enables a differentiation of the ionic radii of Np(III) and Np(IV) in these organometallic environments of 0.08 Å. Complex NpCp₄ shows even a closer contact around the Np atom establishing a trigonal planar coordination environment which is again 0.03 Å smaller but offering further redox chemistry opportunities.

Indeed, potassium reduction at low temperatures of NpCp₄ leads to the formation of very dark-brown crystals of a complex assigned as [K(2.2.2-cryptand)][Np(Cp')₃] K[Np(Cp')₄]; these can be isolated but are less thermally stable than the formally Np(II) complex [Np(L⁴)₃(dme)] previously reported by us; single crystals of the putative Np(V) complex K[Np(Cp')₄] do not survive for long enough to be encapsulated for radiological protection prior to the collection of diffraction data.

The results presented show that neptunium cyclopentadienyl chemistry can show significant deviations from its uranium congeners, in sharp contrast to previous assertions, and the resulting spectroscopic, redox, and structural investigations provide a significant and deeper understanding of minor actinide chemistry.

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**References**

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